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3,062,645

SENSITIZATION OF PHOTOGRAPHIC EMULSIONS TO BE DEVELOPED WITH p-PHENYLENEDIAMINE DEVELOPING AGENTS

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This invention relates to the sensitization of photographic silver halide emulsions which are to be developed with p-phenylenediamine developing agents.

This application is a continuation-in-part of my application Serial No. 642,381, filed February 26, 1957, and now abandoned, which is a continuation-in-part of my application Serial No. 319,615, filed November 8, 1952, now U.S. Patent 2,784,090.

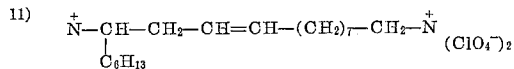
My prior Patent 2,784,090 describes the stabilization with certain organic compounds of mercury, of silver halide emulsions sensitized with onium compounds. Such emulsions may be developed with Elon-hydroquinone developing agents to form black-and-white images, or with p-phenylenediamine developing agents in the presence of color-forming compounds, either in the emulsion or in the developing solution. These color-forming compounds couple with the oxidation product of the p-phenylenediamine developing agent to form dye images.

It is known that certain cationic surface-active agents such as N-dodecyl triethyl ammonium bromide and N-dodecyl pyridinium bromide are not effective in increasing the speed of a silver halide emulsion when it is developed with a p-phenylenediamine developing agent (British Patent 566,314).

I have found, however, that the bis-quaternary ammonium salts in which the cationic ammonium group is linked through the nitrogen atom by a bivalent organic radical containing a chain (including a ring) of at least four (and preferably at least seven) atoms, to the nitrogen atom of another quaternary ammonium salt group, are quite effective in increasing the speed of the silver halide emulsion when the emulsion is exposed and developed with a p-phenylenediamine developing agent in the presence of a compound which couples with the oxidation product of the p-phenylenediamine developing agent.

The bis-quaternary ammonium salts used according to my invention are described, for example, in Carroll and Allen U.S. Patent 2,288,226. Typical compounds are:

- (1) Decamethylene - bis - 2 - phenylpyridazolum-p-toluene sulfonate
- (2) N,N' - trimethylenedioxyethylpyridinium perchlorate
- (3) Hexamethylene-bis-oxymethylpyridinium perchlorate
- (4) 1,10 - decamethylene - bis - 1,3,5 - trimethyl pyrazolum perchlorate
- (5) 1,10 - decamethylene - bis - triethylammonium perchlorate
- (6) Decamethylene - bis - 2,6 - dimethylpyridinium perchlorate
- (7) Tetradecamethylene-bis-pyridinium perchlorate
- (8) Decamethylene-bis-pyridinium bromide
- (9) Decamethylene - bis - 2 - methyl - 5 - ethylpyridinium perchlorate
- (10) Decamethylene - bis - oxymethylpyridinium perchlorate



- (12) 1,4-butylene-bis-pyridinium perchlorate
- (13) Pentamethylene-bis-pyridinium perchlorate

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- (14) n-Hexylene-bis-pyridinium perchlorate
- (15) n-Heptylene-bis-pyridinium perchlorate

The photographic emulsions which I use are of the developing-out type and best results have been obtained with gelatino-silver bromiodide emulsions. However, emulsions of varying halide content may be used.

The emulsions may be chemically sensitized by any of the accepted procedures, in addition to or in combination with the sensitizing with onium compounds. The emulsions may be digested with naturally active gelatin, or sulfur compounds may be added such as those described in Sheppard U.S. Patents 1,574,944 and 1,623,499, and Sheppard and Brigham U.S. Patent 2,410,689.

The emulsions may also be treated with salts of the noble metals such as ruthenium, rhodium, palladium, iridium and platinum, all of which belong to group VIII of the periodic table of elements and have an atomic weight greater than 100. Representative compounds are ammonium chloropalladate, potassium chloropalladate and sodium chloropalladate, which are used for sensitizing in amounts below that which produces any substantial fog inhibition, as described in Smith and Trivelli U.S. Patent 2,448,060, and as anti-foggants in higher amounts, as described in Trivelli and Smith U.S. Patents 2,566,245 and 2,566,263.

The emulsions may also be chemically sensitized with gold salts as described in Waller and Dodd U.S. Patent 2,399,083, Damschroder U.S. Patent 2,597,856, and Yutzy and Leermakers U.S. Patent 2,597,915. Suitable compounds are potassium chloraurate, potassium aurithiocyanate, potassium chloroaurate, auric trichloride and 2-aurosulfobenzothiazole methachloride.

The emulsions may also be chemically sensitized with reducing agents such as stannous salts (Carroll U.S. Patent 2,487,850), polyamines such as diethylene triamine (Lowe and Jones U.S. Patent 2,518,698), polyamines such as spermine (Lowe and Allen U.S. Patent 2,521,925), or bis-(β-aminoethyl) sulfide and its water-soluble salts (Lowe and Jones U.S. Patent 2,521,926).

The bis-quaternary ammonium salts are effective in the presence or absence of optical sensitizing dyes. Both unsensitized emulsions and emulsions sensitized with cyanine or merocyanine dyes or both may be treated with the quaternary ammonium salts according to my invention.

The bis-quaternary ammonium salts may be used in the silver halide emulsion in concentrations ranging from .02 to 4 grams per gram mole of silver halide in the emulsion.

My invention will be further illustrated by reference to the following specific examples:

EXAMPLE 1

A high-speed gelatino-silver bromiodide emulsion containing 0.24 mole of silver halide per liter was digested with a sulfur compound such as disclosed in Shepard U.S. Patent 1,574,944, and potassium chloroaurate, and divided into several portions. One portion was used as a control. To a second portion there was added .75 gram per mole of silver halide of compound 7. To a third portion there was added 3 grams per mole of silver halide of 4-hydroxy-6-methyl-1,3,3a,7-tetrazaindene. To portions of the latter portion there were added various amounts of compound 7. All of these portions were then coated on film base, chill-set and dried. After exposure in an Eastman-type Ib sensitometer for 1/25 second, the films were processed for fifteen minutes in the following solution:

Benzyl alcohol	cc	10
4 - amino-N-ethyl-N-(β - sulfonamidoethyl)-m-toluidine	grams	11
Sodium sulfite (des.)	do	2

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Sodium hexametaphosphate -----do-----	2
Sodium carbonate (des.) -----do-----	35
Sodium thiocyanate -----do-----	0.2
Potassium bromide -----do-----	15
Sodium hydroxide -----do-----	16
8-amino-1-naphthol-3,6-disulfonic acid -----do-----	10
Water to 1 liter.	

The control coating and the coating to which the various addenda had been added were then dried and the results of speed, gamma and fog determinations were found to be as follows:

Compound	grams/mole	Speed	Gamma	Fog
Control.....		333	1.26	.20
Compound 7.....	.75	338	1.28	.61
4-hydroxy-6-methyl-1,3,3a,7-tetraindene (II).....	3.0	342	1.24	.26
Compound 7.....	.75	353	1.48	.27
II.....	3.0	353	1.59	.28
Compound 7.....	2.25			
II.....	3.0			

The speed number used in this table is $100(1 - \log E)$, where E is the exposure in meter candle seconds of light of daylight quality, required to produce a developable density of 0.30 greater than fog: thus an increase of 30 units in speed corresponds to double the sensitivity, an increase of 100 units to 10 times, and so on.

These results show that an appreciable speed increase is obtained when the emulsion is developed in a p-phenylenediamine developer in the presence of a coupler compound. In this case the dye formed by coupling is soluble and is removed from the emulsion during processing but the example illustrates the principle of developing in the presence of a coupling compound.

EXAMPLE 2

A high-speed gelatino-silver bromiodide emulsion was chemically sensitized with sulfur and gold compounds as in Example 1 and optically sensitized to red light, and a cyan color former added in a manner similar to that described in Example 1 of U.S. Patent 2,367,531 using a cyan coupler similar to those described in that patent. To various portions of this emulsion the bis-quaternary ammonium salts shown in the following table were added, and the emulsions were coated on a cellulose acetate film support, dried, exposed on an intensity scale sensitometer and processed as described in "Journal of the Society of Motion Picture and Television Engineers," 61, No. 6, December 1953, pages 672 to 676. This processing involves development directly in a color-forming developer containing a p-phenylenediamine developing agent. The results indicated in the following table were obtained:

Compound	Grams/mole	$\Delta D_{min.}$	ΔSpeed
Control.....			
Compound 6.....	2	+ .08	+ .16
Do.....	4	+ .14	+ .18
Control.....			
Compound 7.....	2	+ .03	+ .20
Do.....	4	+ .08	+ .22
Compound 8.....	1	+ .02	+ .18
Do.....	2	+ .02	+ .18
Compound 9.....	2	0	+ .16
Do.....	4	+ .05	+ .26
Compound 11.....	2	+ .02	+ .12
Do.....	4	+ .10	+ .22
Control.....			
Compound 10.....	1	+ .02	+ .10
Do.....	2	+ .03	+ .15
Control.....			
Compound 12.....	2	+ .06	+ .18
Compound 13.....	2	+ .10	+ .18
Compound 14.....	2	+ .06	+ .16
Compound 15.....	4	+ .22	+ .28

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In this table $\Delta D_{min.}$ indicates change in minimum density compared to the control, and Δ speed indicates change in speed in log E units measured at 0.2 density above fog compared to the control. It will be seen from the table that in every case, the speed is increased when the bis-quaternary ammonium salt is used in the emulsion.

EXAMPLE 3

The use of the following bis-pyridinium compounds in color photography is illustrated in this example.

- I. 4,11-diaza-3,12-dioxotetradecane-1,14-bis-(pyridinium perchlorate)
- II. 3,14-diaza-2,15-dioxohexadecane-1,16-bis-(pyridinium perchlorate)
- III. 7,14-diaza-6,15-dioxoeicosane-1,20-bis-(pyridinium perchlorate)
- IV. 12,19-diaza-11,20-dioxotriacontane-1,30-bis-(pyridinium perchlorate)
- V. 12,23-diaza-11,24-dioxotetatriacontane-1,34-bis-(pyridinium perchlorate)
- VI. 5,12-diaza-3,14-dioxa-4,13-dioxohexadecane-1,16-bis-(pyridinium perchlorate)
- VII. 13,20-diaza-11,22-dioxa-12,21-dioxodotriacontane-1,32-bis-(pyridinium perchlorate)
- VIII. 5,12-dioxa-6,11-dioxohexadecane-1,16-bis-(pyridinium perchlorate)
- IX. 11,22-dioxa-12,21-dioxodotriacontane-1,32-bis-(pyridinium perchlorate)

A sulfur- and gold-sensitized gelatino-silver bromiodide emulsion was ripened to maximum sensitivity. To this emulsion was added an optical sensitizing dye that extended the light sensitivity to 6000-7000 Å. and a hydrophobic cyan color former suitably dispersed in a high boiling organic solvent. A portion of this liquid emulsion received no further treatment; to another portion was added one of the compounds described below. Both portions were coated on film support, and the dry films were exposed to red light in an intensity scale sensitometer. The exposed films were processed in reversal Color Process 1 and in the 5248 Negative Color Process 2 with the results shown in the following table. Color process 2 was carried out as described by Hanson and Kisner JSMPTE 61, 667-701 (1953), for Color Negative Film, Type 5248, involving the steps of color development, fixation, silver bleaching and final fixation.

Color process 1 was carried out at 75° F. as follows:

- (1) Negative development -----minutes-- 10
- (2) Reversal flash exposure.
- (3) Color development -----do----- 15
- (4) Silver bleaching -----do----- 8
- (5) Fixing -----do----- 3

- The negative developer had the following composition:
- | | |
|--|------|
| Water, 90° F. (32° C.) -----liters-- | 1.0 |
| Sodium hexametaphosphate -----grams-- | 2.0 |
| N-methyl p-aminophenol sulfate -----do----- | 6.0 |
| Sodium sulfite, desiccated -----do----- | 50.0 |
| Hydroquinone -----do----- | 6.0 |
| Sodium carbonate, monohydrated -----do----- | 35.0 |
| Potassium bromide -----do----- | 2.0 |
| Sodium thiocyanate -----do----- | 1.5 |
| 0.5% solution of 6-nitrobenzimidazole nitrate -----cc----- | 12.0 |
| 0.1% solution of potassium iodide -----cc----- | 10.0 |

The color developing solution above had the following composition:

- | | |
|--|------|
| Water, 70 to 80° F. (21 to 27° C.) -----liters-- | 1.0 |
| Benzyl alcohol -----cc----- | 6.0 |
| Sodium hexametaphosphate -----grams-- | 2.0 |
| Sodium sulfite, desiccated -----do----- | 5.0 |
| Trisodium phosphate -----do----- | 40.0 |
| Potassium bromide -----do----- | 0.25 |

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0.1% solution of potassium iodide	cc	10.0
Sodium hydroxide	grams	6.5
(4-amino-N-ethyl - N - [β - methanesulfonamido-ethyl] - m - toluidine sesquisulfate monohydrate	grams	11.33
Ethylenediamine sulfate	do	7.8
Citrazinic acid (2,6 - dihydroxyiso - nicotinic acid)	grams	1.5

The silver bleaching solution above had the following composition:

Water 90° F. (32° C.)	liters	1.0
Potassium dichromate	grams	5.0
Potassium ferricyanide	do	70.0
Potassium bromide	do	20.0

The fixing baths above had the following composition:

Water, 80° F. (27° C.)	liters	1.0
Sodium thiosulfate, pentahydrate	grams	150.0
Sodium bisulfite	do	20.0

Table

	Color Process 1 (Reversal) Speed Increase (Log E) ¹	Color Process 2 (Negative) Speed Increase (Log E) ²
Control		
Compound I 2.0 g./mole AgX	+0.25	+0.24
Control		
Compound II 2.0 g./mole AgX	+0.10	+0.16
Control		
Compound III 0.5 g./mole AgX	+0.16	+0.14
Control		
Compound IV 2.0 g./mole AgX	+0.06	+0.04
Control		
Compound V 2.0 g./mole AgX	+0.15	+0.16
Control		
Compound VI 2.0 g./mole AgX	+0.16	+0.15
Control		
Compound VII 2.0 g./mole AgX	+0.18	+0.18
Control		
Compound VIII 4.0 g./mole AgX	+0.14	+0.18
Control		
Compound IX 2.0 g./mole AgX	+0.06	+0.08

¹ Determined by measuring the shift of the reversal dye curve on the Log E axis at a given density below maximum density.

² Determined by measuring the shift of the negative dye curve on the Log E axis at a given density above minimum density.

p-Phenylenediamine developers other than those listed in the examples above may be employed in my process. For example, developers such as N,N-diethyl-p-phenylenediamine, N,N-dimethyl-p-phenylenediamine, 2-amino-5-diethylaminotoluene hydrochloride, 4-amino-N-ethyl-N(β -methanesulfonamidoethyl)-aniline and other similar developers may be employed.

The couplers which are used in my process may be incorporated either in the developing solution as described, for example, in U.S. Patents 1,969,479, 2,271,238 and 2,362,598, or they may be incorporated in the emulsion layer as described, for example, in U.S. Patents 2,298,443, 2,367,531, 2,423,730 and 2,600,788. The color-forming compounds described in these patents are suitable for use according to my invention.

The silver halide emulsions containing the bis-quaternary ammonium salts may be silver bromide, silver iodide, silver chloride or mixed silver halide emulsions. The dispersing agent for the silver halide may be gelatin or other suitable colloidal material such as collodion, albumen, cellulose derivatives or synthetic resins.

It will be understood that I contemplate as included within my invention all modifications and equivalents falling within the scope of the appended claims.

I claim:

1. A light-sensitive silver halide emulsion sensitized

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with a bis-quaternary ammonium salt a quaternary ammonium salt group of which is linked through its quaternary nitrogen atom directly to the quaternary nitrogen atom of the other quaternary ammonium salt group, by a linear chain of at least four atoms, said emulsion containing a coupler compound of the class consisting of phenolic and 5-pyrazolone coupler compounds capable of coupling with the oxidation product of a p-phenylenediamine silver halide developing agent to form a dye.

2. A light-sensitive silver halide emulsion sensitized with a bis-quaternary ammonium salt a quaternary ammonium salt group of which is linked through its quaternary nitrogen atom directly to the quaternary nitrogen atom of the other quaternary ammonium salt group, by a linear chain of at least four atoms, said emulsion containing a 5-pyrazolone coupler compound capable of coupling with the oxidation product of a p-phenylenediamine silver halide developing agent to form a dye.

3. A light-sensitive silver halide emulsion sensitized with a bis-quaternary ammonium salt a quaternary ammonium salt group of which is linked through its quaternary nitrogen atom directly to the quaternary nitrogen atom of the other quaternary ammonium salt group, by a linear chain of at least four atoms, said emulsion containing a phenolic coupler compound capable of coupling with the oxidation product of a p-phenylenediamine silver halide developing agent to form a dye.

4. A method of increasing the speed of a gelatino silver halide emulsion which comprises sensitizing said emulsion with a bis-quaternary ammonium salt a quaternary ammonium salt group of which is linked through its quaternary nitrogen atom directly to the quaternary nitrogen atom of the other quaternary ammonium salt group, by means of a linear chain of at least four atoms, exposing said emulsion and developing it with a p-phenylenediamine silver halide developing agent in the presence of a coupler compound of the class consisting of phenolic and 5-pyrazolone coupler compounds capable of coupling with the oxidation product of said developing agent to form a dye, thereby forming a dye image in the emulsion layer in the region of development.

5. A method of increasing the speed of a gelatino silver halide emulsion which comprises sensitizing said emulsion with a bis-quaternary ammonium salt a quaternary ammonium salt group of which is linked through its quaternary nitrogen atom directly to the quaternary nitrogen atom of the other quaternary ammonium salt group, by means of a linear chain of at least four atoms, exposing said emulsion and developing it with a p-phenylenediamine silver halide developing agent in the presence of a phenolic coupler compound capable of coupling with the oxidation product of said developing agent to form a dye, thereby forming a dye image in the emulsion layer in the region of development.

6. A method of increasing the speed of a gelatino silver halide emulsion which comprises sensitizing said emulsion with a bis-quaternary ammonium salt a quaternary ammonium salt group of which is linked through its quaternary nitrogen atom directly to the quaternary nitrogen atom of the other quaternary ammonium salt group, by means of a linear chain of at least four atoms, exposing said emulsion and developing it with a p-phenylenediamine silver halide developing agent in the presence of a 5-pyrazolone coupler compound capable of coupling with the oxidation product of said developing agent to form a dye, thereby forming a dye image in the emulsion layer in the region of development.

7. The process of claim 4 wherein the coupler compound is present in the emulsion prior to exposure.

8. The method of claim 4, in which the pyridinium salt is decamethylene-bis-2,6-dimethylpyridinium perchlorate.

9. The method of claim 4, in which the pyridinium salt is tetradecamethylene-bis-pyridinium perchlorate.

10. The method of claim 4, in which the pyridinium salt is decamethylene-bis-pyridinium bromide.
11. The method of claim 4, in which the pyridinium salt is decamethylene-bis-2-methyl-5-ethylpyridinium perchlorate.
12. The method of claim 4, in which the pyridinium salt is decamethylene-bis-oxymethylpyridinium perchlorate.

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